# MERCURY IN SOLIDS AND SOLUTIONS BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

## 1.0 SCOPE AND APPLICATION

1.1 Method 7473 is designated for the determination of mercury (CAS No. 7439-97-6) in solids, aqueous samples, and digested solutions in both the laboratory and field environments. Integration of thermal decomposition sample preparation and atomic absorption detection reduces the total analysis time of most samples to less than five minutes in either the laboratory or field setting. Total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials as well as in aqueous wastes and ground waters can be determined without sample chemical pretreatment using this method, except as noted. Alternatively, this method can be used for the detection of total mercury from total decomposition sample preparation methods, such as Method 3052, or for detection of extracted or leached mercury compounds or species from methods such as the SW-846 3000 series methods (as detailed in Chapter Three).

NOTE: For unique circumstances when mercury could be bound in silicates or other matrices that may not thermally decompose, validation of direct analysis of the solid should be confirmed with total decomposition with an EPA approved method (such as Method 3052) and analysis with this method.

## 2.0 SUMMARY OF METHOD

2.1 Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated, releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.7 nm as a function of mercury concentration.

2.2 The typical working range for this method is 0.05 - 600 ng. The mercury vapor is first carried through a long pathlength absorbance cell and then a short pathlength absorbance cell. (The lengths of the first cell and the second cell are in a ratio of 10:1 or another appropriate ratio.) The same quantity of mercury is measured twice, using two different sensitivities (see Figure 1), resulting in a dynamic range that spans at least four orders of magnitude.

2.3 The instrument detection limit (IDL) for this method is 0.01 ng total mercury.

## 3.0 DEFINITIONS

3.1 Thermal Decomposition: Partial or complete degradation of sample components using convection and conduction heating mechanisms resulting in the release of volatile

components such as water, carbon dioxide, organic substances, elements in the form of oxides or complex compounds, and elemental gases.

3.2 Amalgamation: The process by which mercury forms a metal alloy with gold.

3.3 Amalgamator: A system composed of gold particles at a high surface area to volume ratio for the purpose of amalgamating mercury vapor.

3.4 Primary Calibration: A complete calibration of the instrument's working range. This calibration is performed initially and when any significant instrumental parameters are changed. For example, in this method a primary calibration should be performed after the decomposition tube, amalgamator, or oxygen tank is replaced.

3.5 Daily Calibration: A calibration performed with minimal standards to ensure that the primary calibration is valid. For example, when two standards within the range of interest are analyzed and agree within 10% of their true value the primary calibration is assumed to be valid.

3.6 Memory Effects: Mercury vapor may remain in the decomposition tube, amalgamator, or absorbance cells and be released in a subsequent analysis resulting in a positive bias. For example, this may result when a low concentration sample is analyzed after a sample of high mercury content.

3.7 Sample Boat: The non-amalgamating thermally stable vessel used for containment and transport of the solid or liquid sample for thermal decomposition.

## 4.0 INTERFERENCES

4.1 In areas where mercury contamination is an existing problem, the background signal may be significantly increased.

4.2 Memory effects between analyses may be encountered when analyzing a sample of high mercury concentration ($\geq$ 400 ng) prior to analyzing one of low concentration ($\leq$ 25 ng). Typically, to minimize memory effects, analyze the samples in batches of low and high concentrations, always analyzing those of low concentration first. If this batching process cannot be accomplished, a blank analysis with an extended decomposition time may be required following the analysis of a highly concentrated sample to limit memory effects.

4.3 Co-absorbing gases, such as free chlorine and certain organics (as indicated in Methods 7470 and 7471), should not interfere due to the release of decomposition products by the decomposition furnace, removal of some decomposition products by the decomposition catalyst, and the selective entrapment of mercury vapor on the amalgamator.

## 5.0 SAFETY

5.1 Refer to Chapter Three for a discussion on safety related references and issues.

5.2 Many mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Extreme care must be exercised in the handling of concentrated mercury reagents. Concentrated mercury reagents should only be handled by analysts knowledgeable of their risks and of safe handling procedures.

## 6.0 EQUIPMENT AND SUPPLIES

6.1 The working scheme of the mercury analysis system is illustrated in Figure 2. The sample introduction device consists of a motorized support with a metal or metal alloy sample boat that is appropriate for solids and liquids. An example of an appropriate boat would be made of nickel with a liquid capacity of 0.5 - 1.0 mL. Once the sample is either manually or automatically dispensed into the sample boat, the boat is mechanically introduced automatically into a quartz decomposition tube. The decomposition tube is heated by two independently programmable ovens, the decomposition and catalyst furnaces, each furnace is capable of maintaining a temperature of at least 750°C. The sample is dried and thermally decomposed in an oxygen environment, releasing mercury vapor. The mercury vapor is transported by oxygen over the amalgamator that traps the mercury. Once the sample is completely decomposed the trapped mercury is desorbed rapidly by heating the amalgamator with the mercury release furnace. The mercury vapor passes through two absorbance cuvette, in series, that are separated by a collection flask outside the optical axis. The flow path through the spectrometer and cuvettes is maintained at approximately 120°C, by a heating unit, to prevent condensation and minimize carry-over effects. A mercury vapor lamp is used as the light source. The detector is connected to a computer for data acquisition and analysis.

6.2 The DMA 80 automatic mercury analyzer (Milestone, Inc.) is the instrument used for the scheme outlined above. It has been tested for use with this method. Other instruments based on these principles may also be appropriate.

6.3 This method is not limited to mercury vapor generation by thermal decomposition. Alternatively, other mercury vapor introduction systems, such as mercury cold vapor generation, may be appropriate. Alternative sample introduction apparatus may be applied after validation with data similar to those in Tables 1 and 2.

6.4 This method is not limited to analyzing total mercury content. This detection scheme can be used for analysis of individual species of mercury that have been separated by an appropriate method or instrument system.

## 7.0 REAGENTS AND STANDARDS

7.1 Reagent water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.2 High purity oxygen gas: High purity oxygen should be interference and mercury free. If the oxygen is possibly contaminated with mercury vapor, a gold mesh filter should be inserted between the gas cylinder and the mercury analysis instrument to prevent any mercury from entering the instrument.

7.3 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg). Stock solutions may also be purchased. Verify the quality of the standard by checking it against a second source standard (Sec. 9.2).

7.4 Mercury working standards: Make successive dilutions of the stock mercury solution to obtain standards containing 100 ppm and 10 ppm. For calibration of the high range, standards of 0, 1, 2, 3, 4, 5, and 6 ppm are recommended. These are prepared by dilution of the 100 ppm standard. For calibration of the low range, standards of 0.00, 0.05, 0.1, 0.2, 0.3, 0.4, and

0.5 ppm are recommended. These are prepared by dilution of the 10 ppm standard. A blank calibration solution is also used for a zero calibration. Acidity of the working standards should be maintained at least 0.15% nitric acid, as also recommended in Methods 7470 and 7471.

NOTE: The concentrations listed above are only recommended concentrations. The concentration of the working standards may need adjustment according to specific instrumental working ranges and/or manufactures' recommendations.

NOTE: The stability of the mercury standards is limited to 24 - 48 hours. Fresh mercury standards must be prepared daily.

7.5 Standard reference material: In place of aqueous mercury standards, solid reference material with a certified value for mercury may by used for calibration.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

8.2 All sample containers must be prewashed with detergents, acids, and reagent water. Glass, plastic, and PTFE containers are suitable in most cases. Polymers are not suitable for samples containing metallic mercury.

8.3 Metallic mercury, some inorganic mercury compounds, and many organic mercury compounds are volatile and unstable. It is advantageous to analyze the samples as soon as possible to determine the total mercury in the sample but in no cases exceed the 28-day limit as defined in Chapter Three of this manual. Non-aqueous samples shall be analyzed as soon as possible. If solid samples are not analyzed immediately, refrigeration is necessary.

9.0 QUALITY CONTROL

9.1 All quality control data should be maintained and available for easy reference or inspection.

9.2 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous 10 samples must be reanalyzed.

9.3 Matrix Spike/Matrix Spike Duplicates (MS/MSDs): At the laboratory's discretion, a separate spike sample and a separate duplicate sample may be analyzed in lieu of the MS/MSD. For each batch of samples processed, at least one MS/MSD sample must be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/MSD is used to document the bias and precision of a method in a given sample matrix. Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols. MS/MSD samples should be spiked at the same level as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set

at ± 20% of the spiked value for precision and ≤ 20 relative percent difference (RPD). After the determination of historical data, 20% must still be the limit of maximum deviation for both percent recovery and relative percent difference to express acceptability. Refer to Chapter One of this manual for guidance.

9.4 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method and then carried through the appropriate steps of the analytical process. These steps may include but are not limited to digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs then the method blank would be considered acceptable. In the absence of project-specific DQOs, if the blank is less than the MDL or less than 10% of the lowest sample concentration for each analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once and if still unacceptable then all samples after the last acceptable method blank must be reprepped and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

9.5 For each batch of samples processed, at least one laboratory control samples must be carried throughout the entire sample preparation and analytical process as described in Chapter One. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or when lacking project-specific action levels, between the low and midlevel standards. Acceptance criteria should be set at a laboratory derived limit developed through the use of historical analyses. In the absence of historical data this limit should be set at ± 20% of the spiked value. After the determination of historical data, ±20% must still be the limit of maximum deviation to express acceptability. If the laboratory control sample cannot be considered acceptable, the laboratory control sample should be re-run once and if still unacceptable then all samples after the last acceptable laboratory control sample must be reprepped and reanalyzed. Refer to Chapter One for more information.

9.6 The method of standard additions can be used to verify linearity or if matrix interference is suspected. Refer to Method 7000 for standard addition procedures.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Primary calibration: 100 µL of a working standard is dosed onto the sample boat. Analytical parameters for drying, decomposition, and wait times as recommended by the manufacturer are chosen for the analysis (Section 11.1). Each standard solution is analyzed twice. For the DMA 80, parameters of 70 seconds drying, 100 seconds decomposition, and 40 seconds wait times (abbreviated 70/100/40) would be chosen for each standard analysis. Typical calibration curves obtained in laboratory conditions are illustrated in Figures 3a and b and a calibration curve obtained in field conditions is illustrated in Figure 4. Conduct curve using standards described in Section 7.4.

10.2 Daily calibration: At least a high and low concentration standard for each working range is analyzed using the analytical parameters as recommended by the manufacturer. The working calibration standards must be measured within 10% of their true value for the curve to be considered valid.

10.3 An alternative calibration using standard reference materials (SRMs) may be used. In this method, an amount of the reference material is weighed (accurate to ± 0.001 g or better) onto a tared sample boat. The analytical parameters chosen are based on the weight, moisture content, and organic content of the soil and should be as similar to the matrix of interest as possible (refer to Sec. 11.1). This procedure is repeated with several different weights of the standard reference material containing mercury concentrations in the desired working range (see Figure 5).

NOTE: Do not dry the standard reference material as indicated on the certificate of analysis unless the SRM was prepared and analyzed that way for mercury certification. Drying may result in loss of mercury that is thermally unstable. Drying a separate sample at the time of analysis and correcting for moisture content is appropriate.

## 11.0 PROCEDURE

11.1 General analytical parameters: the analytical parameters depend on the sample size and matrix and are instrument specific. The following table shows the guidelines given for the DMA 80. Consult the operating manual for manufactures' recommendations.

Analytical parameters as recommended by Milestone, Inc. for the DMA 80.

| Sample Type | Maximum Capacity | Drying Time (s) [1] | Decomposition Time (s) [1] | Wait Time (s) |
|---|---|---|---|---|
| Aqueous | 500 µL or 1000 µL[2] | = [0.7 s * vol. (µL)] | 100 | 40 |
| Solid (dry) | 500 mg | 10 | = [0.4 s * wt. (mg) + 100 s] | 40 |
| Solid (moist) | 500 mg | = [0.7 s * wt (mg) * % water content] | = [0.4 s * wt. (mg) + 100 s] | 40 |
| Solid (high organic content) | 500 mg | = [0.7 s * wt (mg) * % water content] | 100 | 40 |

[1] The variability of some matrices requires calculating the drying and decomposition times.
[2] Maximum sample size is dependent on the volume of the sample boat. Typical sample boat sizes are either 0.5 or 1.0 mL.

11.2 Sample analysis: For solids, a homogenized amount of the sample is weighed (to ± 0.001 g or better) onto a tared sample boat. The sample boat is inserted into the instrument with appropriate clean techniques. The analytical parameters chosen are based on the weight, moisture content, and organic content of the soil (refer to Sec. 11.1). For example, for 200 mg of sediment with a water content of 45%, the parameters for the DMA 80 would be: 63/180/40. For aqueous samples and previous prepared samples (using appropriate SW-846 3000 series methods), a known volume of the sample is dosed onto the sample boat (3, 4). The analytical parameters chosen are based on the volume of the sample dosed (refer to Sec. 11.1). For example, for 200 µL of prepared sample, the parameters for the DMA 80 would be: 140/100/40.

11.3 Field analysis: With a stable power supply, this method can be transported to the field for direct sample analysis without acid digestions.

11.4 Construct a calibration curve by plotting the absorbances of the standards versus nanograms of mercury. Determine the peak height or peak area of the sample from the chart and

calculate the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed as detailed in Section 9.0 of this method. Samples exceeding the calibration range should be diluted and reanalyzed. Refer to Section 10.0 for additional guidance on calibrating the instrument.

## 12.0 DATA ANALYSIS AND CALCULATIONS

Calculate metal concentrations: (1) by the method of standard addition, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 13.0 METHOD PERFORMANCE

13.1 This method has been validated with both solid samples and digests of solid samples. National Institute of Standards and Technology (NIST) Solid Standard Reference Materials (SRMs) were selected for there homogeneity and availability. The selected SRMs encompass various chemical forms of mercury, including biological forms, geological forms, and contaminated environmental forms. The SRMs were analyzed directly as the solid and as the digested sample as prepared by Method 3052. These results are summarized in Table 1.

Field capabilities of this instrumental method were tested. Direct analysis of various SRMs were performed in a field setting. A summary of the results is given in Table 2. Field analysis with this instrumental method resulted in the data in Table 2. Using this method randomly collected field soil samples were tested. A sample was collected and homogenized in approximately ten minutes and was analyzed in triplicate in an additional 15 minutes. Field data of randomly collected soil samples indicate that typical % RSD of less than 10% can be achieved, however this is dependent on many factors including concentration of mercury and homogeneity of the sample.

13.2 The following documents may provide additional guidance and insight on this method and technique:


13.2.1 Salvato, N. and Pirola, C.; Analysis of Mercury Traces by Means of Solid Sample Atomic Absorption Spectrometry. *Mikrochimica Acta.* Vol. 123, 63 - 71, 1996.

13.2.2 Walter, P.J., and Kingston, H.M.; "The Fate of Mercury in Sample Preparation", The Pittsburgh Conference, Atlanta, GA, March 1997, paper #1223.

13.2.3 Kingston, H.M., Walter, P.J., Chalk, S., Lorentzen E., and Link, D.; "Chapter 3: Environmental Microwave Sample Preparation: Fundamentals, Methods, and Applications" in *Microwave Enhanced Chemistry*; Kingston, H.M. and Haswell, S., Eds.; American Chemical Society, Washington DC, 1997.

13.2.4 Milestone, Inc., DMA 80 Operating Manual, 160B Shelton Rd., Monroe, CN 06468.


## 14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution

prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society.

## 15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society.

## 16.0 REFERENCES

1. Boylan, H.M., Walter, P.J., and Kingston, H.M.; “Direct Mercury Analysis: Field and Laboratory Validation for EPA Method 7473".

## 17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 and 2, Figures 1 through 5, and a method procedure flow diagram.

TABLE 1

LABORATORY ANALYSIS RESULTS (MEAN ± 95% CONFIDENCE INTERVAL) OF DIRECT AND DIGESTED (METHOD 3052) ANALYSES OF VARIOUS NIST SRMs USING THE DMA 80 (MILESTONE, INC.)
(Ref. 1)

| Standard Reference Material | Direct Analysis (ng/g) | Digested Sample Analysis (ng/g) | Certified Value (ng/g) |
|---|---|---|---|
| Apple Leaves NIST SRM 1515 | 48.3 ± 2.4 | NA | 44 ± 4 |
| Citrus Leaves NIST SRM 1572 | 100 ± 12 | 97 ± 9 | 80 ± 20 |
| Estuarine Sediment NIST SRM 1646 | | 75.2 ± 4.9 | 65.7 ± 8.7 |
| 63 ± 12 | | | |
| Oyster Tissue NIST SRM 1566a | 67.1 ± 3.2 | NA | 64.2 ± 6.7 |
| Coal Fly Ash NIST SRM 1633b | 139 ± 6 | 132 ± 12 | 141 ± 19 |
| Buffalo River SedimentNIST SRM 2704 | 1,450 ± 24 | 1,450 ± 26 | 1,440 ± 70 |
| Montana Highly Contaminated Soil NIST SRM 2710 | 33,100 ± 310 | 33,400 ± 230 | 32,600 ± 1,800 |

NA: Not analyzed
$n \geq 3$

TABLE 2

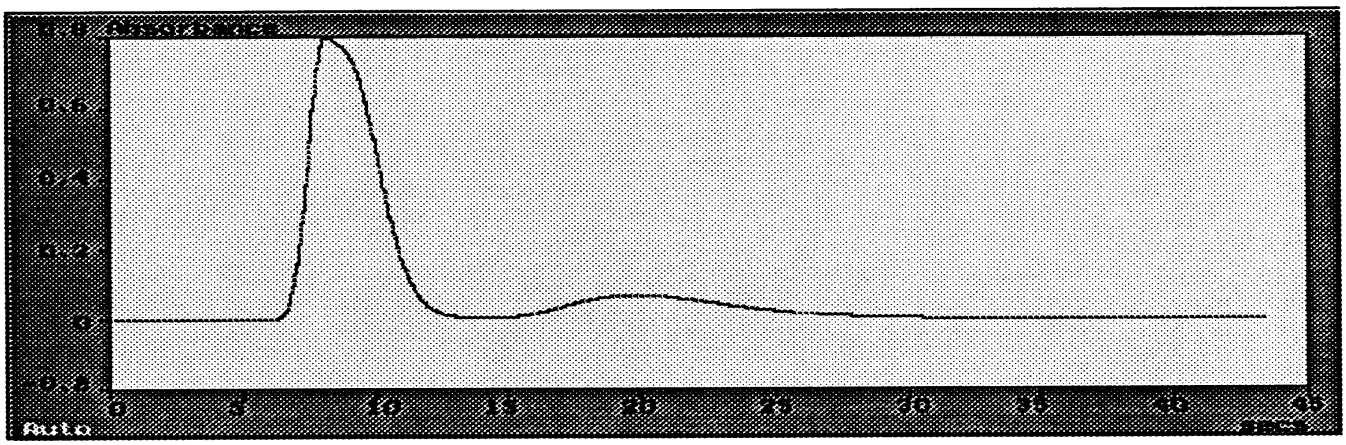
FIELD ANALYSIS RESULTS (MEAN ± 95% CONFIDENCE INTERVAL) OF DIRECT ANALYSES OF VARIOUS NIST SRMs USING THE DMA 80 (MILESTONE, INC.)
(Ref. 1)

| Standard Reference Material | Direct Analysis (ng/g) | Certified Value (ng/g) |
|---|---|---|
| EstuarineSediment NIST SRM 1646 | 74.7 ± 2.4 | 63 ± 12 |
| Oyster Tissue NIST SRM 1566a | 68.0 ± 2.0 | 64.2 ± 6.7 |
| Coal Fly Ash NIST SRM 1633b | 139.2 ± 2.2 | 141 ± 19 |

FIGURE 1

SPECTRAL OUTPUT OF DMA 80

The two individual peaks correspond to the two absorbance cells of different sensitivities. The maximum intensity of the long pathlength cuvette (low range cell) occurs at ~8 seconds and the maximum intensity of the short pathlength cuvette (high range cell) occurs at ~20 seconds.



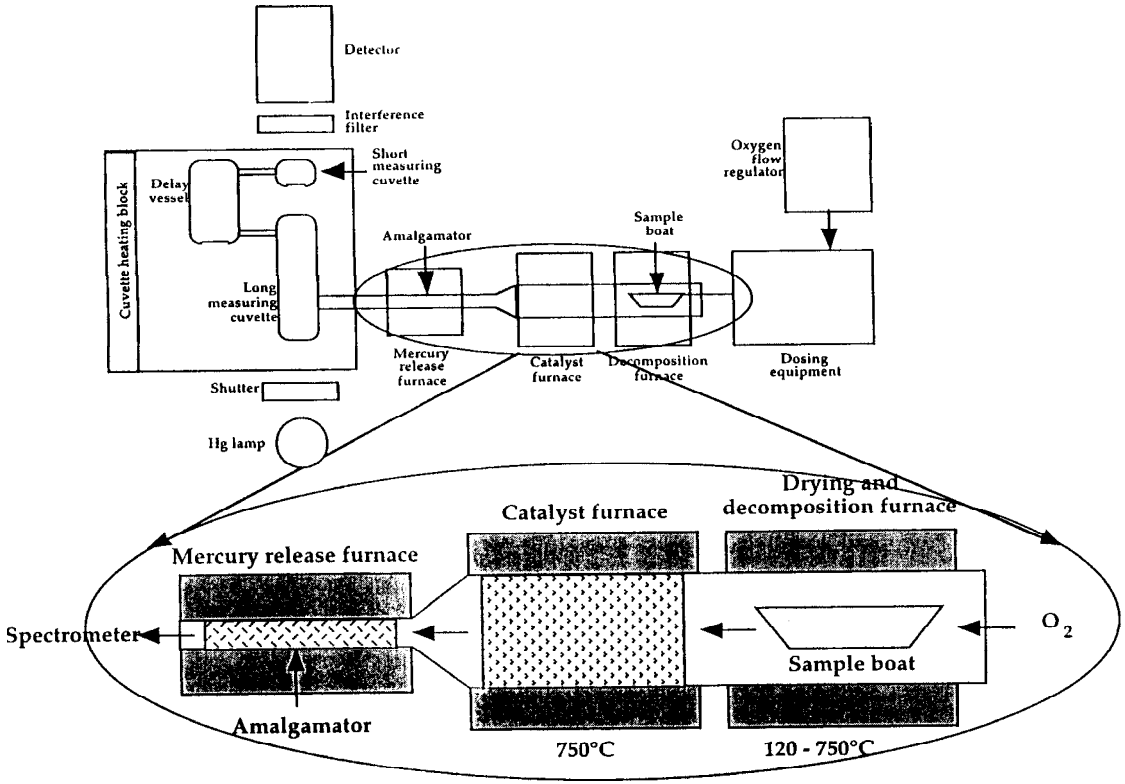


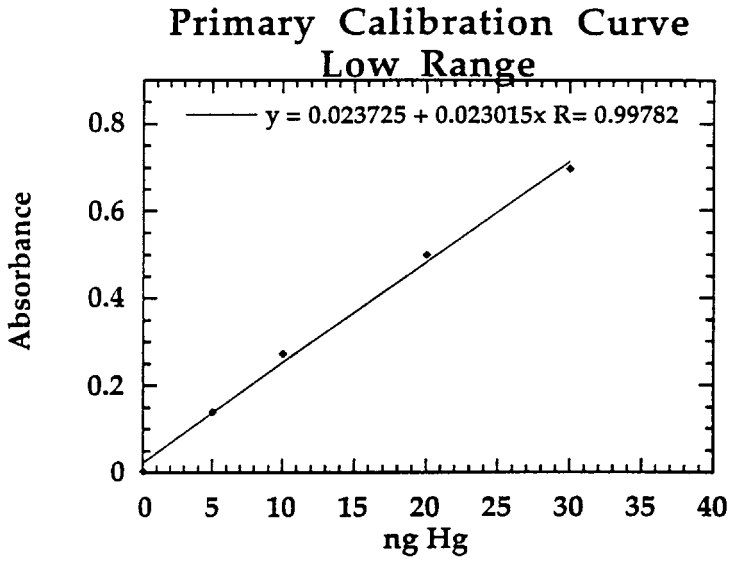

FIGURE 2

DIAGRAM OF THE MERCURY ANALYSIS SYSTEM

FIGURES 3a AND 3b

PRIMARY CALIBRATION CURVES USING THE DMA 80

The low range curve (3a) corresponds to the long pathlength cell. The high range curve (3b) corresponds to the short pathlength cell.



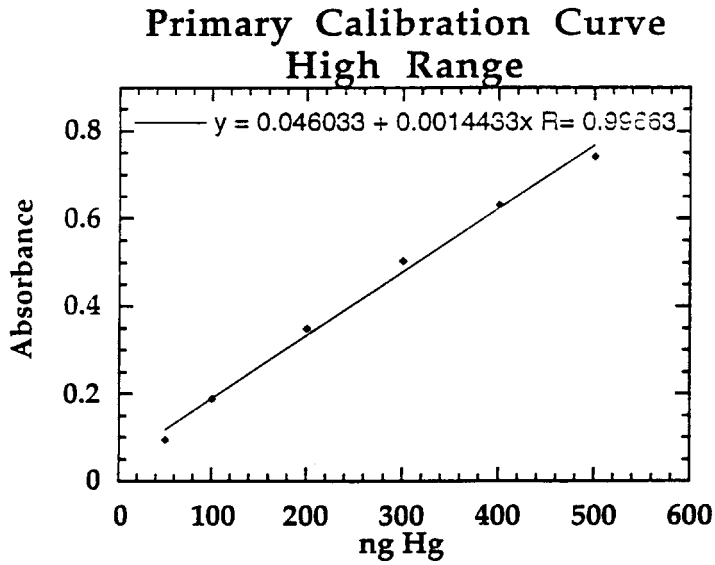



FIGURE 4

PRIMARY CALIBRATION CURVE USING THE DMA 80 IN FIELD ANALYSIS CONDITIONS

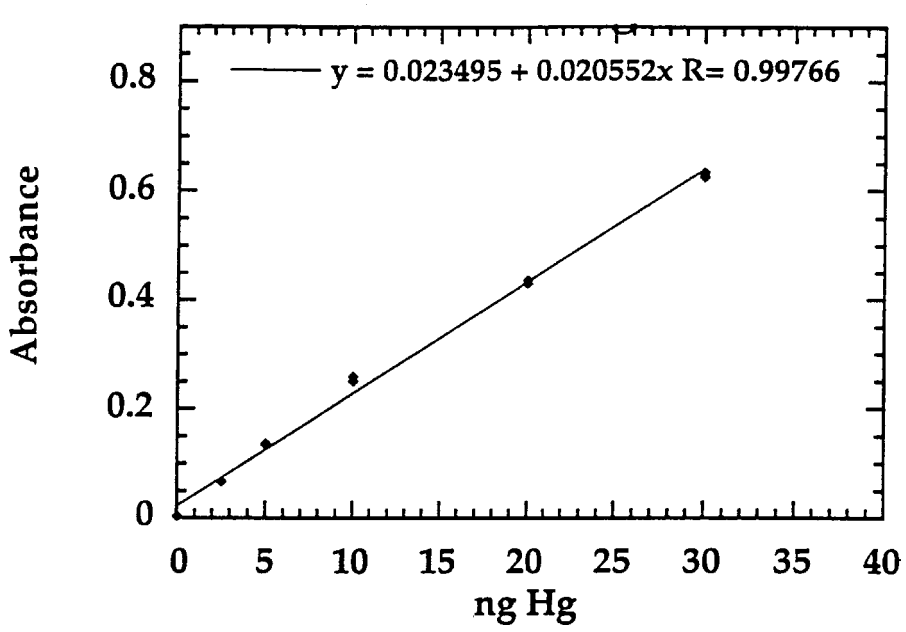
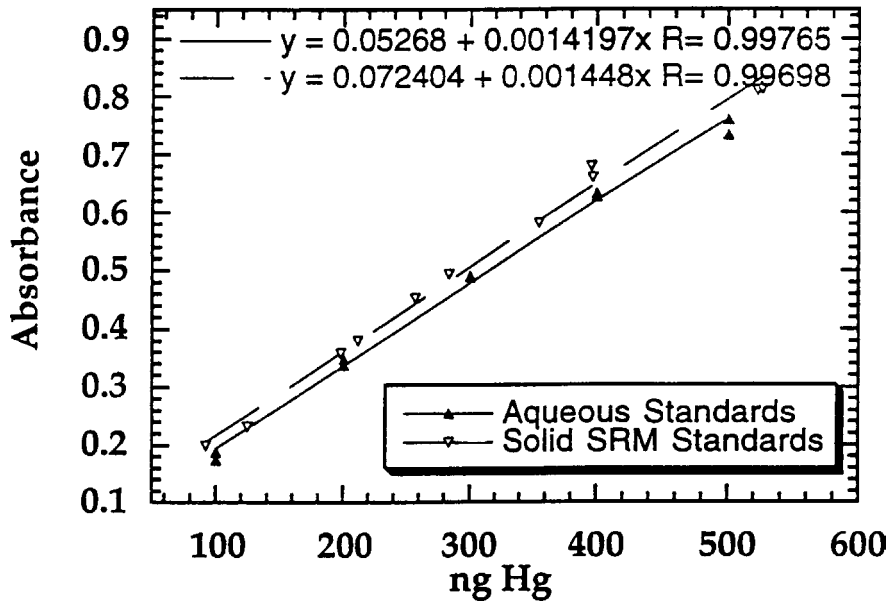


FIGURE 5

PRIMARY CALIBRATION CURVES USING THE DMA 80 -
COMPARISON OF THE CALIBRATION USING AQUEOUS STANDARD SOLUTIONS AND
SOLID NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY STANDARD
REFERENCE MATERIAL 2704 (BUFFALO RIVER SEDIMENT)



MERCURY IN SOLIDS AND SOLUTIONS BY THERMAL DECOMPOSITION, AMALGAMATION, AND ATOMIC ABSORPTION SPECTROPHOTOMETRY